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## Description

The present invention relates to granular detergent activator compositions with improved low temperature activity, granular detergent compositions containing them and a process suitable for producing them.

5 It is well known to incorporate into detergent compositions bleaching compounds such as perborates and other peroxy bleaches and to activate the bleaches in situ using activators for these bleach compounds. The activators must be prevented from coming into contact with the bleach so as to reduce or eliminate reaction of the activator with the bleach compound prior to dissolution of the entire detergent composition in water. This may be done by providing the bleach and bleach activator in separate compositions or by  
10 forming the activator into dry granules with binder, the granules being one component in the dry particulate detergent composition.

One example of the former method is described in EP-A-0170791 in which the bleach activator is compressed into a tablet with other ingredients, including an alkane polyphosphoric acid, a binder and, optionally, a conventional tablet disintegration aid, i.e. a water-insoluble, water-swellable compound. Even  
15 with such disintegration aids the tablets disintegrate too slowly and are not satisfactorily dispersed throughout the water to which they are added. It is inconvenient from the point of view of manufacture since the tableting process is multi-stage and from the point of view of packaging the detergent compositions and for the consumer to have separate compositions.

It is preferred to provide the activator in the form of granules. Upon dissolution in water the granules are  
20 intended to release the activator so as to activate the bleach compound. It is generally intended that this should occur at relatively low wash temperatures (typically 50°C) and so the amount of activator, and its method of granulation, must be such that the desired activity is achieved at the chosen temperature.

The detergent powdered composition will contain a large number of components in addition to the surfactant and bleach components. For instance typical compositions may contain cellulose derivatives,  
25 sequestering agents such as ethylene diamine tetra acetic acid or salts thereof or phosphonic acid sequestering agents, sodium sulphate, sodium silicate, and phosphates or polyphosphates.

It is already known to use some of these materials to form the granules of the activator. There are several methods currently used for granulating the activator.

In one method, such as the method that is said to be preferred in GB-A-2,053,998, particulate activator  
30 is granulated using triphosphate. For instance a saturated aqueous solution of potassium triphosphate may be sprayed on to a blend of particulate activator and particulate sodium triphosphate. Unfortunately this makes it inevitable that the detergent composition contains large amounts of phosphate and this may be undesirable for environmental reasons.

In a second method the activator is granulated using a melt of detergent components, for instance as  
35 described in GB-A-1,557,768, GB-A-1561333, EP-A-0062523 or EP-A-0106634. The resultant granules can then only be used in detergent compositions with which the granulating detergent is compatible, and this therefore restricts the potential use of the granulated activator composition.

In a third method the particulate activator is granulated by compaction of a wet mix of the binder and the activator, e.g. by extrusion through a die or between rollers followed by chopping to the desired size as  
40 in EP-A-0075818.

That specification suggests using a water-insoluble but water swellable disintegration aid, but such materials do not lead to satisfactory disintegration of the granules or do not do so quickly enough at low temperatures, especially when quite high amounts of binder are used.

Another problem with such processes is that it is a multi-stage process and the extrusion and chopping  
45 steps can be time consuming and energy-expensive and the ratios of the amounts of the components cannot be varied at will. In practice the amount of binder has to be below 10% by weight. Such low amounts of binders may be disadvantageous for several reasons, firstly because the granules may have insufficient mechanical strength so that they may be degraded during subsequent processing producing fumes which are a health hazard and which settle out in the particulate detergent and secondly because it  
50 may often be desirable to incorporate a higher amount of the binder material as a component having functions other than as a binder in the detergent compositions.

In DE-A-2048331 (and US-A-3789002) bleach activator granules are produced by mixing dry particles of the activator, which is usually tetraacetylglycoluril, with inorganic salts containing water of hydration and then moistening the blend with water or a solution of granulating aid, which is selected from inorganic salts,  
55 organic binders and detergent compounds. No mixtures of such granulating aids are specifically exemplified. The granules are then coated with water-insoluble solid coating substances such as magnesium oxide.

The granulating aid is present in the final granules in an amount in the range 1-20% by weight but usually less than 10%. The problem with using an aqueous solution or dispersion of organic binder is that

such aqueous mixtures are viscous and difficult to handle especially at high concentrations. This limits the amount of the granulating aid that can practically be incorporated into the granules since the addition of large amounts of water renders the blend into a pasty mixture which cannot be handled, or the liquid must be added over an extended period, which is undesirable, and the process becomes uneconomic because of the large energy requirements for drying the granules. The low amounts of organic binder that can be used may be insufficient for satisfactory strength properties.

An improvement of the process in DE-A-2048331 is described in EP-A-0037026 where, instead of incorporating all of the organic binder in solution or dispersion in the water used to moisten the dry bleach activator, part or all of the binder is mixed as dry particles with the activator particles, before the moistening takes place. Again, water-swellaable materials can be incorporated into the granules as disintegration aids, but these do not give satisfactory increases in the rate of disintegration of the granules in use, especially at low temperatures.

In DE-A-3247893 special polyphosphonic acids and their water soluble salts are used stabilisers for bleach activators. It is stated that the stabilisers can be co-granulated with the bleach activator by mixing dry stabiliser with dry activator particles and then granulating by any of the conventional processes e.g. by spraying a dry blend with a solution of an organic binder. These all suffer from the disadvantages described above and the inclusion of particulate polyphosphonate does not affect the rate of disintegration of the granules significantly.

The method described in EP-A-0037026 and DE-A-2048331 has the advantages that it does not cause environmental pollution and the granulate can be used in a wide variety of detergent compositions. However it has the disadvantage that the amount of binder has to be low and this can result in the granules breaking during manufacture, causing processing difficulties. The product has, despite this, been widely accepted as being very successful.

However we have now observed that despite its success the product does not achieve its full potential during use at low temperatures. In particular we believe that during a normal low temperature wash cycle a significant amount of the activator is not released into solution. This problem becomes particularly serious with decreasing wash temperature and when the composition is used in cold fill machines where the water temperature can be less than 20 °C.

It would therefore be desirable to produce a granulated composition that gives improved activity, especially at low wash temperatures and with cold-fill wash cycles. It would also be desirable to be able to increase the amount of binder above the levels proposed in EP-A-0037026 without causing the composition to have inadequate activity.

According to the invention a new process for the production of a granulated detergent bleach activator in which particles of activator and of organic binder are dry blended, moistened during mixing by an aqueous solution and then dried and is characterised in that the solution contains a water soluble granule disintegration aid comprising a sequestering agent.

In the present specification the "standard composition" is one particular example of a typical composition made by the process described in EP-A-0037026. It is formed by mixing dry particles of tetraacetylenediamine (TAED) bleach activator (100 parts) with dry particles of sodium carboxymethyl-cellulose (CMC) binder (5.53 parts) in a suitable mixer (e.g. a Shugi Flexomix (trade mark)) or a Lodge ploughshare mixer for 3 minutes and then adding about 23 parts water. Mixing is continued for a further 2 minutes after which the product is discharged and dried for 15 minutes at 60 °C using a fluid bed drier.

The process can produce granule compositions in which the presence of the disintegration aid causes substantial increase in the activity of the composition when dissolved in water at 20 °C containing perborate and a detergent base in a simulation of a cold-fill system (PA 20). The objective of the invention here is to reduce the quantity of undissolved activator collecting in the sump of the machine by effecting rapid release of the available peracid. In such a simulated test the product of the process show an increase in activity of more than 1.3 times compared to the compositions free of the granulation aid after 2 minutes of the test and an increase of more than 1.3 after 5 minutes of the test.

The 2 and 5 minutes activities at 20 °C (PA20, t=2 and t=5) are measured by the following test. The granulated composition (3g) is added to 1 litre of distilled water containing 100 ppm of calcium ions and 40g of a spray dried detergent base (ECE detergent base obtained from the Society of Dyers and Colourists, Bradford, W. Yorks), thermostatically controlled at 20 °C. Sodium perborate tetrahydrate (12g) is added and the timer set to zero. Aliquots of 50 ml are taken at 2, 5 min and titrated as described above. The results are expressed as moles of peracid liberated per g of activator as a percentage of the theoretical quantity available.

The presence of the disintegration aid in the process also causes substantial increase in the activity of the composition when dissolved in water at 40 °C containing perborate (PA40). The process can produce

compositions having a 30 minute activity which is more than double, preferably more than four times and most preferably more than ten times, for instance twenty five to fifty times, the activity of the corresponding compositions free of granulation aid. The process can produce, further more compositions are those which have a 5 minute activity more than 1.2 times and preferably more than 1.5 times, for instance 1.7 to 2.5 times the 5 minute activity of the corresponding granules free of disintegration aid.

The 5 and 30 minute activities at 40 °C (PA40 t=5 and t=30) are a measure of activity throughout the wash cycle and are measured by the following test. The granulated composition (1g) is added to 1 litre of distilled water containing 100 ppm of calcium ions and 1 drop of sodium dodecylbenzene sulphonate as a wetting agent, thermostatically controlled at 40 °C. Sodium perborate tetrahydrate (5g) is added and the timer set to zero. Aliquots (50ml) were removed at 5 and 30 minutes and titrated at 0 °C against 0.1M sodium thiosulphate in the presence of potassium iodide and glacial acetic acid. The end-point of the titration is determined using Vitex (trade mark) indicator. Duplicate titrations are carried out for each time interval.

The quantity of per acid found by each titration (PA40) is expressed as the number of moles of peracid/g activator, as 100% active material, i.e., a correction is made for the binder content.

The granule disintegration aid can be any water soluble material comprising sequestering agent that will promote rupture of the granules and exposure of the activator particles to the water. It is advantageous because the granule disintegration aid has stabilising properties upon the peracid species formed on the reaction of the bleach and the activator. By using these stabilising compounds it is possible to maintain the peracid activity over an extended period in the wash as compared to compositions free of the compounds. Thus the 30 minute activity at 40 °C (as defined above) can be maintained at, or close to, the 5 minute activity at 40 °C.

The disintegration aid comprises a sequestering agent or mixture of sequestering agents. It may comprise an amino carboxylic acid sequestering agent, for instance nitrilo triacetic acid or ethylene diamine tetra acetic acid or diethylene triamine penta acetic acid (or salts thereof) or a low molecular weight anionic polymer formed from ethylenically unsaturated monomers e.g. unsaturated carboxylic acid or sulphonic acid monomers, such as acrylic acid, but preferably the disintegration aid comprises a phosphonic acid sequestrant or stabiliser.

The disintegration aid may comprise, in addition to such sequestering agents, water-soluble inorganic salts, such as alkali metal or alkaline earth metal salts, preferably sodium, potassium calcium or magnesium salts or mixtures. The salts may be the water-soluble sulphates, carbonates or halides, usually chlorides, mixtures can be used. Particularly suitable examples are sodium sulphate and magnesium sulphate.

Although it has been proposed to co-granulate phosphonic acid derivatives with bleach activators, for example in GB-A-2053998 and GB-A-1561333 those examples have used different binders in their processes which have the problems explained above and there has been no suggestion how to improve granules bound by organic binder. Although the process in DE-A-3247893 uses an organic binder, it is applied from aqueous solution (or dispersion) which has the disadvantages mentioned above. Furthermore the phosphonic acid is used as part of the dry materials and will not become dispersed within the granule, so that it will not have any significant effect on the rate of disintegration and appearance of activator activity.

Any of the phosphonic acid compounds conventionally present in detergents as stabilisers or sequestrants may be used including ethylene diamine tetra (methylenephosphonic acid) (EDTMP) for instance as the free acid or as the hexa sodium salt, diethylene triamine penta (methylenephosphonic acid) (DTPMP), hexamethylene diamine tetraphosphonic acid (HMDTP), nitrilotri(methylenephosphonic acid) (NTMP) or its sodium salt or hydroxyethyl-1,1-diphosphonic acid (HEDP). The phosphonic acids may be present as in the granules as free acid or as acceptable and active salts e.g. with ammonia, alkali metal (generally sodium) or alkaline earth metal (generally calcium or magnesium) or as complexes with, for instance, zinc or aluminium. The phosphonic acids have the further property that they enhance the stability of the peracid species formed during the reaction of the bleach and the bleach activator.

The binder must be an organic polymeric binder that can be a natural or synthetic polymer and can be water swellable or water soluble. Synthetic binders include polyacrylates, polymaleates and polyvinyl pyrrolidones, which may be cross linked, e.g., the cross linked polyvinyl pyrrolidone sold under the trade mark Gafdis. Preferably the binder is a natural binder (including derivatives thereof), most preferably a starch binder, generally a starch ether, or a cellulose binder, generally a cellulose ether or ester. Particularly preferred binders are carboxymethyl cellulose CMC.

The weight ratio of activator:binder may be from 98:2 to 30:70, generally 98:2 to 50:50. It is particular advantage of the invention that it is not necessary to keep the amount of binder below 10% and although this can be done particularly preferred compositions have ratios of 89:11 to 55:45.

The amount of granulating aid(s) will depend on the granulation aid(s) being used and on the binder and the amount of binder but is generally in the range 1 to 20%, preferably 2 to 15% and most preferably 3 to 10% by weight of the activator, binder and granulating aid(s). In particular, where an inorganic component is employed the cation should contribute from 0.165% by weight of the granule, preferably 0.3 to 2.0%, most preferably 0.4 to 1.5%.

Although the product granules preferably consist substantially only of the activator, binder and disintegration aid(s) other components of the final detergent may be included in the process if desired in any suitable amounts. Preferably however such additions provide less than 10% and generally less than 5% by weight of the granules. One component that can usefully be included in the granules is optical brightening agent since its incorporation in the granules avoids the problems associated with incorporating it in the remainder of the detergent composition. For instance it may be damaged by the spray drying to which the remainder of the composition is generally subjected. Another component that can conveniently be co-granulated is an antisudsing (anti foaming) or foam stabilising agent. Other components that may be cogranulated are other components of detergent compositions such as surfactants, anti redeposition acids, builders, pigments or dyes and enzymes.

The particulate activator is preferably tetra acetyl ethylene diamine but may be any of the known detergent bleach activators, such as those described in GB-A-2,048,930 or EP-A-0037026. Other preferred activators include polyacetyl mono-, di-, or polysaccharides such as penta acetyl glucose, sulphonates such as isononanoyl oxybenzene sulphonate, nonyl benzoates, glycourils such as tetra acetyl glycouril, N-acyl amides, acylated diketopiperazines, and other N-acyl amines.

The activator should be provided in the form of small particles generally having an average particle size in the range 50 to 500  $\mu\text{m}$ , preferably 100 to 300  $\mu\text{m}$ . Preferably substantially none of the particles has a size above 300  $\mu\text{m}$  or, at the most, 500  $\mu\text{m}$ . The particulate binder preferably has an average particle size below 200 microns, generally below 100 microns and is preferably free of particles above 200  $\mu\text{m}$  in size.

The granules preferably have an average particle size of between 300 and 1500  $\mu\text{m}$ , most preferably 500 to 1000  $\mu\text{m}$ . Preferably substantially none of them have a size above 2000  $\mu\text{m}$  and preferably not above 1700  $\mu\text{m}$ . Preferably none of the granules have a size below 50  $\mu\text{m}$  and most preferably none have a size below about 125  $\mu\text{m}$ . Granules that are too fine are preferably separated from the granules and recycled for further granulation, often after crushing. A particular advantage of the invention is that the large amounts of binder that can be used minimise the risk of formation of fines.

In the process it is preferred that the aqueous solution used to moisten the particulate blend is substantially free of organic binder, in order to avoid the problems with handling viscous solutions or dispersions, mentioned above. Thus substantially all the organic binder is provided as dry particles to be mixed with the particulate activator. Furthermore, best results are achieved if substantially all the water soluble granule disintegration aid(s) is dissolved in the aqueous solution. We have found that by this process the disintegration aid is fully distributed throughout the granules so that it has optimal effects on the disintegration of the granules upon their addition to water.

The resultant granules can be incorporated in conventional detergent compositions that contain a suitable bleach component that is activated by the activator. The preferred bleaches are peroxy compounds, especially perborates such as sodium perborate tetrahydrate but others that can be used include sodium perborate monohydrate or sodium percarbonate.

The detergent may contain, in addition to surfactants, detergent builders and anti-redeposition aids, enzymes, anti-sudsing agents, foam stabilisers, optical brightening agents, pigments, dyes and perfumes, sequestrants, halide salts such as sodium bromide, manganese salts such as manganous sulphate and inert fillers such as sodium sulphate or silicate. A particular advantage of the invention is that it is not necessary to include phosphates, although they may be included if desired. The amount of activator, based on the total weight of the detergent, may be conventional or may be less than usual, because of the increased activity. Typical amounts are 1 to 5% based on the total detergent, or 10 to 50% based on the bleach.

The following examples are batchwise preparations suitable for the laboratory and larger scale production by employing techniques familiar to those skilled in the art. Granulation can also be effected on a large scale by the simultaneous addition of the individual components, in the same ratios as those given in the following examples, into a high speed continuous agglomerator e.g. a Feexomix.

#### Reference Example

The standard composition is made by the following process:-  
Into a suitable mixing machine is weighed:  
TAED 1012g

CMC 56g

The dry components are mixed for 3 minutes after which Water 233g is added, whilst mixing is continued, over 2 minutes. The product is then discharged and dried for 15 minutes at 60 °C using a fluid bed drier.

5 Examples 1 - 11 and Comparative examples A & B

Using the same general technique as in the reference example, particulate bleach activator and particulate binder are mixed dry in various proportions and are then sprayed with an aqueous solution of the granule disintegration aid or aids (i.e. any inorganic salt, sequestering agent and/or urea). The nature of the  
10 disintegration aids and relative amounts of the components in the granules produced are shown in accompanying tables 1 and 2.

Compositions made by these general techniques were sieved to separate a fraction of 1000 to 1700 µm and the granules were then tested for activity by the method described above.

The values of PA40 (t=5) and PA40 (t=30) and the value of PA20 (t=2) and PA20 (t=5) for the  
15 granules made in the examples are measured by the techniques described above. The values obtained are related to the standard composition for which PA40 (t=5), PA40 (t=30), PA20 (t=2) and PA20 (t=5) all are given the value 1.0. The results are shown in Tables 1 and 2, in which the following abbreviations are used:

	TAED	= tetra acetylene diamine
	Na	= sodium ions
20	Mg	= magnesium ions
	SO <sub>4</sub>	= sulphate anion
	CO <sub>3</sub>	= carbonate anion
	Cl	= chloride anion
	EDTMP	= ethylenediaminetetra(methylene phosphonic acid)
25	NTMP	= nitrilotris (methylenephosphonic acid)
	DTPMP	= diethylenetriaminepenta(methylene phosphonic acid)
	CMC	= sodium salt of carboxymethylcellulose.
	DTPA	= diethylenetetramine pentaacetic acid.

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TABLE 1  
Examples

		1	2	3	4	A	B
5							
10	TAED	60	60	90	60	60	60
	NaSO <sub>4</sub> , 10H <sub>2</sub> O	-	-	-	-	-	5
	MgSO <sub>4</sub> , 7H <sub>2</sub> O	7	7	-	-	-	-
15	EDTMP	6	1	3.8	-	-	-
	DTPA	-	-	-	5	-	-
	Urea	-	-	-	-	5	-
	CMC	20	22	4	23	22	23
20	Water						
				to 100%			
	PA40 t=5	2.0	1.8	1.7	1.5	1.2	0.9
25	t=30	35	35	34	9	4	2.5
30	PA20 t=2	2.6	2.0	1.4	1.5	0.7	0.6
	t=5	2.1	1.6	1.3	1.3	0.9	0.8

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TABLE 2  
Examples

		5	6	7	8	9	10	11
5								
10	TAED	82	86	85	85	85	60	88
	Na	0.8	0.8	1.0	1.0	1.0	-	-
	Mg	-	-	-	-	-	0.7	0.7
15	SO <sub>4</sub>	1.7	1.7	2.1	-	-	2.8	2.8
	Cl	-	-	-	-	1.5	-	-
	CO <sub>3</sub>	-	-	-	1.3	-	-	-
	EDTMP	-	-	4.8	4.8	4.8	7.0	1.2
20	NTMP	4.0	-	-	-	-	-	-
	DTPMP	-	4.8	-	-	-	-	-
	CMC	4.5	4.0	4.0	4.0	4.0	20	6.0
25	Water	to 100%						
30	PA20 t=2	1.8	1.7	1.5	1.4	1.4	2.6	2.0
	t=5	1.3	1.5	1.5	1.4	1.5	2.1	1.6

35 From these examples it will be apparent that an activator granule formed with a mixture of a binder and sequestering agent offers a significant improvement in both the immediate availability of peracid from the coated activator and the level throughout the wash part of the cycle, as compared to the standard composition and to compositions containing urea alone as the disintegration aid or an inorganic salt alone (comparative examples A and B). The combination of phosphonic acid with inorganic salt gives an even  
40 further improvement in the immediate availability of peracid at 20°C i.e. under cold-fill conditions.

#### Comparative Example C

45 A granulated mixture was made by using components in the same proportions as for example 10 but by mixing all the ingredients dry and then adding pure water to the blend during mixing (instead of using a solution of EDTMP and magnesium sulphate). The activities at 20°C (PA20) were t = 2, 0.68 and t = 5, 1.06. This shows that the granules made with solid disintegration aid have much lower activities under cold fill conditions than those made with a solution of disintegration aid.

#### Comparative examples D to G

Granules of activator were formed using a range of conventional table disintegration aids, i.e. which are water-swellaable, instead of the water-soluble disintegration aids used in the present invention. A process similar to that used in the reference example was used but replacing part of the binder with the disintegrant.  
55 The type and amount (weight percentage based on total dry ingredients) of disintegrant and PA20 values are given in the table below:



TABLE 3

	D	E	F	G
5 Avicell (micro-crystalline cellulose)	0.5	2.0	-	-
10 Ac-di-sol (modified cellulose gum)	-	-	0.5	2.0
PA20 t=2	0.53	0.62	0.86	0.95
t=5	0.78	0.78	0.90	0.95

Table 3 shows that conventional disintegration agents of the water-swellaable type produce granules which have even worse PA20 values than the standard composition.

#### 20 Wash Tests

The importance of the improved availability of peracid which can be obtained as a result of the invention is demonstrated by the results of carefully controlled wash tests presented in Table 3 below:

25 Wash tests were carried out at 40°C and 50°C (HLCC programmes 5 and 4 respectively) on red wine stains using ECE detergent base and 12% sodium perborate tetrahydrate. Hoover computer control 1100 machines were used with a controlled water hardness of 250 ppm calcium carbonate. Activator granule additions were adjusted to give 3% TAED by weight in the detergent mixture. Stain removal was measured by reflectance using a tristimulus colour analysing computer and the results are shown in Table 3.

30 The value of  $\Delta R\%$  in the table is the percentage difference in stain removal as measured by reflectance from a washed swatch of stained cloth, with the value of  $\Delta R\%$  for the standard composition being given the value 0.

Table 4

	<u>EXAMPLE</u>	<u><math>\Delta R\%</math></u>	<u>40°C</u>	<u>50°C</u>
35	5	+10	+17	
40	6	+14	+17	
	7	+7	+18	
	8	+5	+12	
	9	+5	+15	
45	10	+15	+17	
	11	+7	+7	

50 These results demonstrate the value of the invention in a practical wash test.

#### Claims

1. A process for the production of a granulated bleach activator in which particles of organic binder material and particles of bleach activator are dry blended, moistened during mixing by an aqueous solution and dried, characterised in that the solution comprises dissolved water-soluble granule disintegration aid comprising a sequestering agent.

2. A process according to claim 1 in which the granule disintegration aid is selected from amino carboxylic acids, phosphonic acids and low molecular weight anionic polymers formed from ethylenically unsaturated monomers, and is preferably a phosphonic acid sequestering agent.
- 5 3. A process according to claim 1 or claim 2 in which the granule disintegration aid also comprises an inorganic salt.
4. A process according to any preceding claim in which the weight ratio of activator: binder is in the range of from 98:2 to 30:70, preferably from 89:11 to 50:50 or to 55:45, and in which the amount of granules disintegration aid is in the range of from 1 to 20% by weight of the total weight of activator, binder and granule disintegration aid, preferably 1 to 15%.
- 10 5. A process according to any preceding claim in which the binder is selected from starch and cellulose binders, preferably carboxymethyl cellulose.
- 15 6. A process according to any preceding claim in which the granules consist substantially only of the activator, binder, disintegration aid and 0 to 10% of other components optionally including optical brightening agent(s) and/or anti-sudsing agents.
- 20 7. A process according to any preceding claim in which the activator is tetra acetyl ethylene diamine.
8. A process according to any preceding claim in which the activator is initially provided in the form of particles having sizes in the range from 100 to 300  $\mu\text{m}$  in size and the granules have an average particle size in the range of 300 to 1500  $\mu\text{m}$  with substantially none of the granules having a size above 1700  $\mu\text{m}$ .
- 25 9. A process according to any preceding claim in which the solution is substantially free of organic binder material.
- 30 10. A process according to any preceding claim in which substantially all of the water soluble granule disintegration aid is dissolved in the aqueous solution.
11. A granule detergent composition containing the product of a process according to any preceding claim, a detergent component and a bleach component.

35 **Patentansprüche**

1. Verfahren zur Herstellung eines granulierten Bleichmittelaktivators, worin Teilchen aus organischem Bindemittelmaterial und Teilchen aus Bleichmittelaktivator trocken vermischt, während des Mischens durch eine wäßrige Lösung angefeuchtet und getrocknet werden, dadurch gekennzeichnet, daß die Lösung ein gelöstes, wasserlösliches Komplexierungsmittel umfaßendes Granulatsprenghilfsmittel umfaßt.
- 40 2. Verfahren nach Anspruch 1, worin das Granulatsprenghilfsmittel unter Aminocarbonsäuren, Phosphonsäuren und anionischen Polymeren mit niedrigem Molekulargewicht, welche aus ethylenisch ungesättigten Monomeren gebildet werden, ausgewählt ist und vorzugsweise ein Phosphonsäurekomplexierungsmittel ist.
- 45 3. Verfahren nach Anspruch 1 oder 2, worin das Granulatsprenghilfsmittel auch ein anorganisches Salz umfaßt.
- 50 4. Verfahren nach einem der vorstehenden Ansprüche, worin das Gewichtsverhältnis von Aktivator zu Bindemittel im Bereich von 98:2 bis 30:70, vorzugsweise von 89:11 bis 50:50 oder bis 55:45 reicht, und worin die Menge an Granulatsprenghilfsmittel im Bereich von 1 bis 20 Gew.-% des Gesamtgewichtes von Aktivator, Bindemittel und Granulatsprenghilfsmittel, vorzugsweise 1 bis 15 %, beträgt.
- 55 5. Verfahren nach einem der vorstehenden Ansprüche, worin das Bindemittel unter Stärke und Cellulosebindemitteln vorzugsweise Carboxymethylcellulose, ausgewählt ist.

6. Verfahren nach einem der vorstehenden Ansprüche, worin die Körnchen im wesentlichen nur aus dem Aktivator, dem Bindemittel, dem Sprenghilfsmittel und 0 bis 10 % von anderen Komponenten, welche wahlweise einen oder mehrere optische Aufheller und/oder Antischaummittel beinhalten, bestehen.
- 5 7. Verfahren nach einem der vorstehenden Ansprüche, worin der Aktivator Tetraacetylthlendiamin ist.
8. Verfahren nach einem der vorstehenden Ansprüche, worin der Aktivator am Beginn in Form von Teilchen zur Verfügung gestellt wird, welche Größen im Bereich von 100 bis 300 µm besitzen, und die Granulate eine mittlere Teilchengröße im Bereich von 300 bis 1500 µm aufweisen, wobei im wesentlichen keines der Granulate eine Größe über 1700 µm besitzt.
- 10 9. Verfahren nach einem der vorstehenden Ansprüche, worin die Lösung im wesentlichen von organischen Bindemittelmateriale frei ist.
- 15 10. Verfahren nach einem der vorstehenden Ansprüche, worin im wesentlichen das gesamte wasserlösliche Granulasprenghilfsmittel in der wässrigen Lösung gelöst ist.
11. Granulatdetergensenzusammensetzung, welche das Produkt eines Verfahrens gemäß einem der vorstehenden Ansprüche, eine Detergensenkomponente und eine Bleichmittelkomponente enthält.

#### Revendications

1. Procédé de production d'un activateur de blanchiment granulé, dans lequel des particules de liant organique et des particules d'activateur de blanchiment sont mélangées à sec, humidifiées durant le mélange par une solution aqueuse et séchées, caractérisé en ce que la solution comprend un auxiliaire hydrosoluble dissous de délitement des granules, qui comprend un agent séquestrant.
- 25 2. Procédé selon la revendication 1, dans lequel l'auxiliaire de délitement des granules est sélectionné parmi les acides aminocarboxyliques, les acides phosphoniques et des polymères anioniques à poids moléculaire bas, formés à partir de monomères insaturés sur le plan éthylène, et est de préférence un agent séquestrant du type acide phosphonique.
- 30 3. Procédé selon la revendication 1 ou 2, dans lequel l'auxiliaire de délitement des granules comprend également un sel minéral.
- 35 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport pondéral activateur : liant est compris dans la plage de 98 : 2 à 30 : 70, de préférence entre 89 : 11 et 50 : 50 ou 55 : 45, et dans lequel la quantité d'auxiliaire de délitement des granules est comprise dans la plage de 1 à 20% en poids du poids total de l'activateur, du liant et de l'auxiliaire de délitement des granules, de préférence entre 1 et 15%.
- 40 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le liant est sélectionné parmi des liants d'amidon et de cellulose, de préférence la carboxyméthylcellulose.
- 45 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel les granules sont constitués pratiquement uniquement par l'activateur, le liant, l'auxiliaire de délitement et 0 à 10% d'autres composants comprenant facultativement un ou des agents de blanchiment optique et/ou des agents antimousse.
- 50 7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'activateur est de la tétraacétyléthylènediamine.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'activateur est initialement fourni sous forme de particules de dimensions comprises dans la plage de 100 à 300 µm et dans lequel les granules ont une granulométrie moyenne comprise dans la plage de 300 à 1 500 µm, pratiquement aucun des granules n'ayant des dimensions supérieures à 1 700 µm.
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9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la solution est pratiquement exempte de liant organique.
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel pratiquement tout l'auxiliaire hydrosoluble de délitement des granules est dissous dans la solution aqueuse.
11. Composition détergente granulaire contenant le produit d'un procédé selon l'une quelconque des revendications précédentes, un composant détergent et un composant de blanchiment.

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